

PATENT SPECIFICATION

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(54) IMPROVEMENTS IN OR RELATING TO BRAZING ALUMINIUM

(71) We, ALCAN RESEARCH AND DEVELOPMENT LIMITED, a Company incorporated under the laws of Canada, of 1, Place Ville Marie, Montreal, Quebec, Canada, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to the joining by brazing of sheet, tube and other forms of aluminium. The term "brazing sheet" is hereinafter employed for convenience to include tube and other forms of aluminium suitable for brazing.

Aluminium brazing sheet having a surface cladding on one or both faces of an aluminium alloy having a melting point which is lower by, say, 30—40°C. than the core of the sheet is extensively used in the production of heat exchangers. The core may be aluminium or an aluminium alloy. This surface layer forms the hard solder by means of which components made from such brazing sheet may be joined together. In the brazing operation the assembly of such components to be joined is subjected to a temperature at which the surface layer is melted without melting the core. In order to be able to achieve that result under industrial conditions without risk there must be a difference in the melting points of the order of 30—40°C.

In order to produce a brazed joint a flux is employed to remove the aluminium oxide coating present both on the surface of the brazing sheet and the aluminium to which it is to be joined. Conventionally the flux employed for the purpose has been a mixture of chloride salts, including alkali metal and alkaline earth metal chlorides. These water soluble materials are corrosive to aluminium in the presence of moisture. Consequently at the end of the brazing

operation the brazed assembly must be subjected to a cleaning operation to remove the water soluble flux. Even so there are usually inclusions of the flux in the metal of the joint which may result in corrosion after a relatively short interval, particularly where the brazed assembly may be subjected to humid conditions.

It is already known to braze aluminium without the use of a flux under vacuum or inert gas conditions, but the capital cost of the equipment employed is very high. Moreover a major disadvantage of the fluxless brazing methods is that much closer tolerances must be observed for assembly than for flux brazing. Any failure to maintain very close tolerances results in the brazed assemblies being rejected due to incompletely filled joints.

It is an object of the present invention to provide a brazing flux for use in the production of an aluminium brazed joint having the characteristics of being non-hygroscopic prior to brazing and substantially insoluble in water after brazing, whilst exhibiting the necessary qualities of becoming reactive at a temperature below the melting point of the hard solder layer and acting as a flux or solvent for aluminium oxide and being substantially unreactive with aluminium whilst in the molten condition.

In the most widely employed brazing sheet the core is clad with a hard solder layer formed of an aluminium-silicon eutectic melting at about 577°C. and therefore the flux employed should become reactive at a temperature below that value.

It has already been proposed in British Patent No. 1,055,914 to produce a flux for soldering aluminium by mixing 53—55% AlF₃ with 47 to 45% KF, within which range a known eutectic point occurs, having a melting point of about 560°C. In this prior proposal the materials are either mixed dry,

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with subsequent addition of water, or the KF is added in aqueous solution. In both alternatives the resultant paste is dried at a temperature below 200°C.

5 The material produced by that method was reported as leaving a brittle, non-hygroscopic residue at the end of the brazing operation. Although the method of production results in an intimate admixture of the soluble KF with the insoluble AlF_3 , there does not appear to be a complete reaction between the fluoride components and the resultant material is hygroscopic and is thus unsuitable for use in aqueous slurry. Slurrying of this material in water would result in solution of KF and consequent possibility of disproportionation of the flux on drying and melting point variability.

10 The flux material of British Patent No. 1,055,914 was recommended for use in inert and non-hygroscopic vehicles, which would obviate the above-mentioned difficulties.

15 However, for many brazing operations, particularly closed heat exchanger assemblies, such as radiators for motor vehicles and evaporators for air conditioners, the conditions preclude the use of resinous binder. In such case the relative absence of oxygen makes it impossible to burn off more than a very slight amount of the carbonaceous material in the brazing operation, so that the flux must be entrained in a vehicle which is substantially completely evaporable. Of such vehicles water is by far the most suitable, both from aspects of cost and operating convenience, since it leaves no residue and requires no oxygen for burn-off.

20 X-ray diffraction examination of the solidified residue of the eutectic mixture of KF and AlF_3 , which occurs at about 45.8% KF and 54.2% AlF_3 , indicates that virtually all the fluoride contents are in the form of K_3AlF_6 and KAlF_4 , which are very sparingly soluble in water and are non-hygroscopic. In fact the fused eutectic consists of these two phases and not of KF and AlF_3 .

25 We have therefore appreciated, in accordance with the present invention, that in order to permit the flux to be employed in the form of an aqueous slurry it is necessary to convert the flux materials essentially into a mixture of insoluble potassium fluoaluminate complexes before application to the hard solder (alloy surface coating of the brazing sheet) and that it should be essentially free of unreacted KF. The simplest and preferred method of obtaining such a mixture is to fuse together AlF_3 and KF in correct proportions, allow the mix to cool and then grind the cooled mass to an appropriately small particle size

to allow it to be suspended in water in the form of a thin slurry. It is found that grinding to -100 mesh (smaller than 150 microns) is generally satisfactory, but it is preferred to grind it to -150 mesh or even -200 mesh (smaller than 104 and 75 microns respectively). It is however possible to prepare K_3AlF_6 and KAlF_4 separately and to mix them in the required proportions. The preparation of KAlF_4 has been described by Brosset in *Z. Anorg. Algern. Chemie.* Vol. 239, pages 301-304 (1938).

Typically the flux material is made up into a thin slurry by the addition of 2 parts of water to 1 part by weight of finely ground flux. A very small amount of surface active agent is found to assist the deposition of a uniform layer of flux on the aluminium surface (which may be the aluminium solder surface or the surface of the aluminium to which the solder is to be joined) and it is preferable to add a very small amount, such as $\frac{1}{2}\%$, of a conventional hydroxyethyl cellulose thickening agent to maintain the flux in suspension. The amount of carbonaceous material is too small to lead to the formation of unacceptable carbon deposits during the brazing operation.

It is preferred that the relative proportions of KF and AlF_3 employed in the preparation of the flux should be as close to the eutectic point as possible. Whilst the melting point shown in the published diagram (*Journal American Ceramic Society*, 49, pages 631-4, December 1966) rises very rapidly if the quantity of KF rises above that required for the eutectic, there is only a slight rise in melting point to about 574°C where the AlF_3 rises above the eutectic up to a total of about 60% (50 moles % AlF_3).

The flux of the present invention is essentially free of unreacted KF and consists essentially of one or more potassium fluoaluminates in such amounts that they are composed of reacted potassium fluoride and reacted aluminium fluoride in proportions of 40-50:60-50. However when the relative proportions of reacted KF to reacted AlF_3 falls below 41:59, KAlF_4 is the only potassium fluoaluminate present.

All percentages and proportions herein are by weight, except where otherwise stated.

It is found that, surprisingly in relation to the above-quoted published data, satisfactory fluxing is effected throughout the quoted range, although the effectiveness of the flux decreases away from the eutectic point.

Small quantities of other alkali- or alkaline-earth metal or zinc fluorides, up

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to a total of about 5 mole %, can be tolerated in the mix from which the flux is prepared by fusion, providing that the melting point of the flux is not raised above that of the hard solder. However, the presence of such fluorides does not appear to confer any benefits by reducing the melting point below that of the KF/AlF_3 eutectic and all have the effect of raising the melting point to some extent even where the KF/AlF_3 proportions have been adjusted to provide optimum melting point conditions.

In preparing the flux by the fusion method from technical grade KF and AlF_3 , the materials in finely ground, dry state are mixed in proportions to yield KF and AlF_3 , within the above relative proportions. The purity of the KF is not critical and technical or commercial grade KF has been found to be satisfactory. The impurities normally associated with technical KF are therefore acceptable and, to facilitate weighing and mixing with the AlF_3 , the KF is ground to at least -100 mesh and should be moisture-free to avoid difficulties in the fusion operation.

In the case of the aluminium fluoride, the effectiveness of the flux appears to diminish with decreasing purity of this component. The best technical results are obtained with pure distilled AlF_3 . On the other hand, a usable flux has been prepared from aluminium fluoride with an AlF_3 content as low as 67%. The purity of commercially available aluminium fluoride depends largely on the method of manufacture and the preferred commercial material is 95% purity aluminium fluoride which is produced by the fluosilicic acid process and is available at reasonable cost. The principal impurity in this material is alumina while the other normally-associated impurities such as sulphates, iron-oxide, silica, etc., are believed to have little effect but should each be less than 0.3%. Aluminium fluorides of lower purity and produced by alternative processes have been used successfully but to ensure consistent success, that is, over a reasonably wide range of furnace brazing conditions, the minimum purity should be 90% AlF_3 .

As stated above, both KF and AlF_3 should be dry before the fusion reaction to avoid the possibility of the hydrolysis of AlF_3 .

Example

Potassium fluoride and aluminium fluoride in a thoroughly dried condition are ground to pass through a 70 mesh screen (smaller than 212 microns). The ground materials are mixed in the proper proportions according to the invention and

mixed intimately. The mixture is then placed in a graphite crucible, which is placed in a furnace at $625^\circ\text{--}650^\circ\text{C}$. As the mixture fuses it is stirred with a platinum stirrer. The molten material is then quickly poured into a mould to solidify.

Flux material made as described above was ground to -200 mesh (finer than 75 microns) and was slurried with water to form a thin slurry as described above and the material was employed in the production of a heat exchanger of the wafer and fin type, produced from hard solder-coated brazing sheet of the type already discussed. The aqueous slurry was applied to the facing surfaces of the assembly at a rate of about 250 gms/sq. metre. With this flux application sound joints were formed when the assembly was subjected to a temperature of about 600°C . in the brazing furnace.

Unlike the conventional chloride fluxes, the fused aluminium fluoride/potassium fluoride complex flux is non-hygroscopic and does not tend to become entrapped in the liquid filler metal. This allows the flux material to be exposed to the atmosphere or to be formed into an aqueous slurry prior to brazing without the problems of oxychloride formation, and permits strong dense corrosion-free joints to be formed.

Whilst the principal advantage of the present invention is that it provides a flux of extremely low solubility, which may be applied as an aqueous slurry and which results in an essentially inactive residue, the flux performs its fluxing function equally well when applied in a resinous vehicle, provided that the brazing operation can be carried out under open conditions, permitting the resinous binder to be burnt away.

Since the material is essentially non-corrosive to aluminium and non-hygroscopic, the use of a flux of this nature opens up the possibility of supplying pre-fluxed brazing sheet, which would be of great value in high volume production of some brazed assemblies.

The resinous vehicle should be of such a nature that it decomposes below the melting point of the flux. However, many resins have this characteristic.

The flux, ground to a size of -100 mesh (smaller than 150 microns) or finer, may be dispersed in a water-soluble or a water-dispersible resin, an example of the latter being Reichold polyester resin STF 355 in combination with a suitable cross-linking agent such as Cymel 300. The flux composition is then spread on the surface of the brazing sheet and stoved at an appropriate temperature to bake the resin to put it into a condition suitable for storage until the brazing operation is to be carried

out. Of course the flux-resin mixture may be applied just prior to brazing in which case the stoving operation can be omitted. Alternatively, a solvent-based resin composition may be employed, such as a solvent-based acrylic resin paint vehicle. A further alternative is to apply both the flux and the resin as dry powders by electrostatic methods with subsequent stoving. The flux should be applied preferably in an amount of 175—350 gms./sq. metre to obtain good results. It is, of course, clear that the flux is only required on those areas of the sheet which will coincide with a joint. In some instances therefore it is sufficient to apply the flux paint composition to selected areas, for example by the employment of a screen printing technique, to achieve economy in materials.

In another use the flux is mixed with a powdered aluminium alloy of the type used as a hard solder for brazing, and with a resinous vehicle. This mixture is spread on components made from aluminium sheet, tube, or other wrought products or from castings, whose surface, unlike that of the brazing sheet described above, has not been clad with a hard solder layer. These coated components may be heated so as to produce on their surface a hard non-hygroscopic layer containing flux, resin and the powdered hard solder. Such components can subsequently be joined together by simultaneously holding them in contact and heating them to, or slightly above, the melting point of the hard solder. In the presence of the flux the molten particles of the hard solder coalesce and form an alloy bond with and between the components. In yet another use the flux-resin coating is spread on both sides of a rolled strip of a hard solder alloy which is then stoved so as to yield brazing stock which may be cut to the required size and inserted between components of uncoated wrought or cast aluminium which are to be brazed together.

When employing conventional water-soluble chloride fluxes, which must be removed after the brazing operation, it has been the practice to quench brazed assemblies in water immediately after removal from the brazing furnace. Where a high strength was required, it was usual to employ a brazing sheet having a core of an alloy whose maximum strength can be developed only by quenching from elevated temperature and by subsequently age-hardening, e.g. AA6063 (Al—Si 0.2—0.6%, Mg 0.45—0.9%).

According to a further feature of the invention there may be employed, as the core alloy for a brazing sheet for use in conjunction with the flux of the present

invention, an aluminium alloy having a melting point above 615°C and which can develop satisfactorily high strength properties when cooled relatively slowly, such as by cooling in air, on removal from the brazing furnace, and is self-ageing, so that an ageing heat treatment step after quenching becomes unnecessary. Thus a self-ageing Al—Zn—Mg alloy, such as AA7104 (Al—Zn 3.8%—Mg 0.8%) may be employed as core alloy, having a melting range of 615°—645°C. This alloy is preferably modified by the inclusion of a graingrowth inhibitor, such as 0.3% Mn. The core alloy is preferably clad with an Al—Si 10% or Al—Si 12% alloy, modified by the addition of 1—2% Zn to reduce the difference in the electro-potential between the core alloy and the cladding alloy to a value of less than 0.1 volt when measured with reference to a saturated calomel electrode in a solution of normal sodium chloride plus 0.1N hydrogen peroxide. The inclusion of the stated amount of zinc has little effect on the melting point of the hard solder Al—Si cladding layer.

WHAT WE CLAIM IS:—

1. A method of producing a brazed joint between aluminium or aluminium alloy components which comprises interposing between the facing surfaces of said components a layer of an aluminium alloy solder of lower melting point than said components, a layer of a flux comprising one or more potassium fluoaluminate complexes essentially free of unreacted potassium fluoride, said fluoaluminates containing reacted KF and AlF_3 in the relative proportions of 40—50:60—50 by weight, said flux being in finely divided form, and heating said components to a temperature above the melting point of said solder and said flux and below the melting point of said aluminium or aluminium alloy.

2. A method according to claim 1 comprising applying said flux in the form of a slurry in an evaporable liquid.

3. A method according to claim 2 wherein said liquid is water.

4. A method according to claim 3 wherein at least one of a pair of facing surfaces of said components is clad with a layer of hard solder.

5. A method according to claim 1 in which a layer of finely divided flux admixed with finely divided aluminium alloy solder is interposed between a pair of facing surfaces.

6. A method according to claim 1 comprising applying said flux as a suspension in a resinous vehicle.

7. A method of producing a brazed aluminium assembly which comprises interposing between the facing surfaces of

5 two aluminium components a flux layer of
finely divided particles consisting
essentially of a fused mixture of fluorides
containing KF and AlF_3 in the relative
10 proportions of 40—50:60—50 by weight, at
least one of said components comprising a
self-ageing aluminium alloy having a
melting point in excess of $615^\circ C$. and
bearing a surface layer of aluminium alloy
15 solder comprising aluminium and 10—12%
Si and 1—2% zinc to reduce the
electropotential between the self-ageing
alloy and the solder alloy to a value below
0.1 volt when measured with reference to a
saturated calomel electrode in a solution of

normal sodium chloride plus 0.1N hydrogen
peroxide and heating said components to a
temperature above the melting point of the
solder alloy and the flux and below $615^\circ C$.

8. The method of Claim 7 in which the 20
self-ageing aluminium is an Al—Zn—Mg
alloy.

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